



Electrocatalytic dechlorination of volatile organic compounds at copper cathode. Part II: Polychloroethanes

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ABSTRACT

Copper is considered as a catalytic electroodic material for the reduction of organic halides for possible application in environmental remediation. In Part I, we have demonstrated that Cu is a good electroodic material in the reduction of polychloromethanes (PCMs). In this second part, we extended the study to geminal polychloroethanes (PCAs) with the aim of understanding whether the catalytic activity and the reduction mechanism observed for PCMs are maintained or significantly affected by molecular structure. To this end, we considered the electroreduction of 1,1,1-trichloroethane (TCA) and 1,1-dichloroethane (DCA), which are the simplest molecules belonging to the homologous series of chloroform and dichloromethane, respectively, at a Cu electrode in DMF under controlled proton availability. Voltammetric investigations point out that PCAs can be sequentially reduced at both GC and Cu. Copper shows modest catalytic effects for TCA and DCA; with respect to GC, E_p at Cu anodically shifts by 210 mV and 76 for TCA and DCA, respectively. In contrast to the reduction of PCMs, Cu exhibits a good electrocatalytic activity only in the presence of acetic acid, HAC, indicating a strong influence of the structure of the polychlorinated molecule. Controlled-potential electrolyses have shown that the reduction mechanism and therefore the intermediates and final products of the reduction process are profoundly affected by the presence of H₂O or HAC. In analogy to what was previously observed for PCMs, sequential hydrodehalogenation leading to ethane as the final product becomes the principal reaction pathway in the presence of HAC. In the presence of H₂O both hydrodehalogenation and dehydrodehalogenation mechanisms are possible. In the latter case the mechanism involves α,β -elimination of H⁺ and Cl[−] and leads to the formation of chlorinated olefins and acetylene.

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1. Introduction

Polychloroethanes (PCAs) have been used for a wide range of industrial applications and, as a consequence of numerous leaks into the environment, they are commonly detected in industrial facilities and waste disposal sites [1]. The half-lives of the lower chlorinated members of the group (1–3 chlorine atoms) under reductive conditions often exceed several decades [2]. To date, biological methods employed for the removal of C₂ polychlorohydrocarbons are successful in the rapid and complete in situ reductive dechlorination of tetrachloroethylene (PCE) and trichloroethylene (TCE), but are inefficient in the case of PCAs. Among PCAs, 1,1,1-trichloroethane (TCA) is a banned chemical due to its particularly aggressive activity in the depletion of ozone and is classified as a possible human carcinogen. Although TCA is susceptible to a variety of natural abiotic and biotic transfor-

mations, the rate of natural transformation is often insufficient to prevent its migration in groundwater, particularly at sites where TCA is co-disposed with other common chlorinated solvents such as PCE and TCE [3]. Common TCA transformation products including 1,1-dichloroethane (DCA), 1,1-dichloroethylene (DCE), vinyl chloride (VC), and chloroethane (CA) all have aqueous solubilities far exceeding that of TCA and are classified as possible human carcinogens. All of these products are susceptible to a variety of degradation processes, but their degradation rates vary widely and in general they can be as persistent as or even more persistent than TCA in groundwater. All these aspects prompted the search for robust degradation methodologies that are faster and more efficient than biological treatments.

Due to the electronegative character of the chlorine atoms in polychlorohydrocarbons, reduction appears as a valid method. Reductive dechlorination can be achieved by chemical means such as reduction at zero-valent metal particles [4] and catalytic hydrodechlorination at noble metal nanoparticles [5] or by electrochemical reduction at both bulk metal [6] and nanostructured metal electrodes [7]. In comparison with the popular relevance

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of the zero-valent metal treatment [8], the electrochemical route presents benefits such as enhanced reduction kinetics with limited consumption of electrodic materials [9], intrinsically milder experimental conditions and higher selectivity. Among the electrodes investigated Ag has shown to be one of the most promising materials, possessing good catalytic properties both in terms of current efficiency and selectivity [10,11]. Recently, also Cu has gained some attention [12,13] not only due to its low price and high availability but also, and principally, because of its good catalytic activity that in some cases resembles that of the more noble Ag [14].

We have shown in Part I of this series [14] that Cu possesses remarkable electrocatalytic properties for the reduction of polychloromethanes (PCMs) allowing their exhaustive dechlorination to methane, especially in the presence of good proton donors. The research reported here was aimed to understand whether the molecular structure of PCA can affect the dechlorination mechanism and/or the catalytic activity of Cu. On this regard, we selected TCA and DCA as the higher homologues of CHCl_3 and CH_2Cl_2 , respectively. A correct rationalization of the reduction mechanism in H_2O is often precluded by a plethora of uncontrollable side reactions and by the difficulty of sampling and analyzing the reaction intermediates and products. In fact, hydrodehalogenation involves both electron and proton transfers and it is helpful to be able to control both of them. To this end, use of an organic solvent with low proton availability may help to better rationalize the involved mechanisms. For this reason DMF was chosen as the reaction medium. Of course transposition of the results obtained at such a medium to an aqueous solution is not straightforward. However, degradation in an aqueous environment might not be the only situation we face. In fact, if the problem is to degrade the existing stock of PCAs, which are by themselves good solvents, electrochemical dechlorination at a catalytic metal electrode can be achieved in bulk by simply enhancing the conductivity with an appropriate supporting electrolyte or in micro-fluidic systems which require a small amount of supporting electrolyte [15]. On the other hand, electrochemical reduction of polyhalogenated pollutants in organic solvents after sequestering treatments might represent an advisable choice. In fact, since PCAs are highly soluble in organic solvents, highly concentrated solutions can be prepared and electrolyzed with high current densities. This means that great amounts of PCAs may be converted to less dangerous or even more valuable products in a reasonably short period of time.

2. Experimental

2.1. Chemicals

DMF (WWR, 99%) was treated with anhydrous Na_2CO_3 and doubly distilled at reduced pressure under a N_2 atmosphere. Tetrapropylammonium tetrafluoroborate (Pr_4NBF_4) (Fluka, >98%) was recrystallised twice from EtOH and dried in a vacuum oven at 70°C . 1,1,1-trichloroethane and 1,1-dichloroethane were high purity reagents purchased from Sigma–Aldrich and were used without further purification.

2.2. Electrochemical instrumentation

Electrochemical measurements were performed on a computer-controlled EG&G PARC Model 273A potentiostat equipped with a digital coulometer. Cyclic voltammetry experiments were carried out in a three electrode cell with a glassy carbon (GC) disc or a Cu disc as working electrode. The counter electrode and the reference electrode were a Pt wire and $\text{Ag}|\text{AgCl}|\text{Me}_4\text{NCl}(\text{sat})$ in $\text{CH}_3\text{CN}/\text{DMF}$ 3/1, respectively. The latter was calibrated after each experiment against the ferrocenium/ferrocene couple. The potentials measured

against the $\text{Ag}|\text{AgCl}|\text{Cl}^-$ reference electrode were converted to the SCE scale, to which all potentials in the paper are referred, by using $E_{\text{Fc}^+/\text{Fc}}^0 = 0.475\text{ V}$ versus SCE in DMF. The working electrodes were built from a 3 mm diameter GC rod (Tokai, GC-20) or from a 2 mm diameter Cu wire (Alfa Aesar, 99.999%) and were cleaned and activated prior to each experiment as previously described [16]. Controlled-potential electrolyses were carried out in a divided cell using a Cu cylinder of 9.5 cm^2 area, a Pt foil as counter electrode and $\text{Ag}|\text{AgCl}|\text{Cl}^-$ as a reference electrode. In all electrolysis experiments reported in this paper a single Cu working electrode was used, which showed to be always catalytically active regardless of the number of experiments or their durations. All experiments were carried out at 25°C .

2.3. Analytical methods

Electrolysis products were analyzed using an HP 6890 gas chromatograph equipped with an HP 5973 mass selective detector (MS) or a flame ionization detector (FID) (Agilent Technologies). Products in the liquid phase were analyzed as headspace samples on a DB-5ms $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$ capillary column using the MS detector, whereas an HP Plot Q $30\text{ m} \times 0.537\text{ mm} \times 0.40\text{ }\mu\text{m}$ capillary column and the FID detector were used for the analysis of the gaseous products (see Supplementary Information for more details). Authentic compounds were used for the identification and quantification, via calibration curves, of all products.

3. Results and discussion

3.1. Cyclic voltammetry

Cyclic voltammetry of TCA and DCA has been carried out in $\text{DMF} + 0.1\text{ M Pr}_4\text{NBF}_4$ at GC and Cu electrodes and the peak potentials (E_p) measured at $\nu = 0.2\text{ V/s}$ are summarized in Table 1. TCA at GC (Fig. 1A) shows three reduction peaks at -2.12 , -2.70 and -2.90 V vs SCE. The first peak is the reduction of TCA, whereas the second coincides with that of pure DCA acquired in the same experimental conditions (Fig. 1A, dashed line). This finding clearly indicates that reduction of TCA yields DCA, which in turn is reduced at a more negative potential. Although no specific experiment has been carried out on ethyl chloride (CA), it is plausible to assume that reduction of DCA yields CA. Thus, the last peak observed for TCA and DCA can be attributed to the reduction of ethyl chloride. The peak potentials of TCA and DCA are very similar to those of CHCl_3 (-2.17 V vs SCE) and CH_2Cl_2 (-2.74 V vs SCE), respectively.

There are two possible mechanisms for the reductive cleavage of organic halides [17]: a stepwise mechanism involving a labile radical anion as an intermediate or a concerted mechanism in which electron transfer and bond rupture occur in a single step. It has

Table 1

Voltammetric data for geminal polychloroethanes (2 mM) in $\text{DMF} + 0.1\text{ M Pr}_4\text{NBF}_4$ in the absence and presence of H_2O or acetic acid (HAc).

Substrate	Proton donor	GC E_p^a (V)	Cu E_p^a	$\Delta E_{p,\text{cat},b}$ (V)
CHCl_2CH_3	–	-2.72	-2.65	0.07
CHCl_2CH_3	H_2O^c	-2.72	-2.58	0.14
CHCl_2CH_3	HAc^d	-2.59	<-2.56	<0.03
CCl_3CH_3	–	-2.12	-1.91	0.21
CCl_3CH_3	H_2O^c	-2.10	-2.04	0.06
CCl_3CH_3	HAc^e	-2.07	-1.25	0.82

^a E_p (vs SCE) measured at $\nu = 0.2\text{ Vs}^{-1}$.

^b $\Delta E_{p,\text{cat}} = E_{p,\text{Cu}} - E_{p,\text{GC}}$.

^c In the presence of 1 M H_2O .

^d In the presence of 6 mM HAc.

^e In the presence of 8 mM HAc.

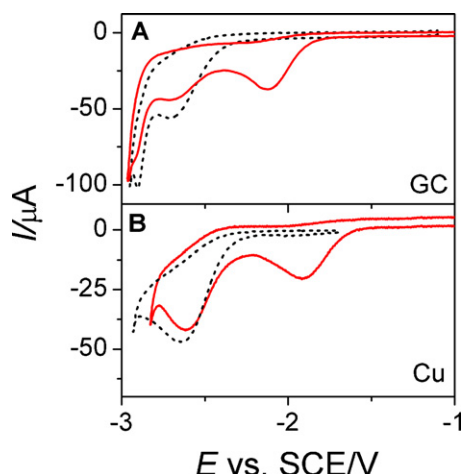
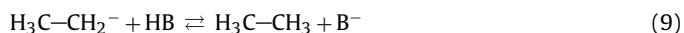
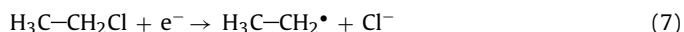
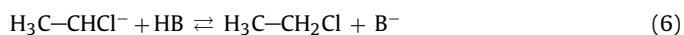
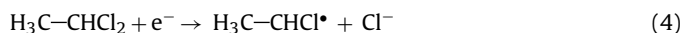
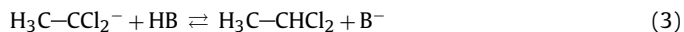
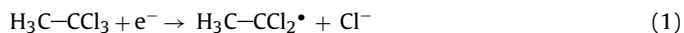


Fig. 1. Cyclic voltammetry of 2 mM CH_3CCl_3 (solid line), 2 mM CH_3CHCl_2 (dashed line), recorded at $\nu = 0.2 \text{ V s}^{-1}$ in DMF + 0.1 M Pr_4NBF_4 at (A) GC and (B) Cu electrodes.

been shown that the transfer coefficient (α) can be used as a convenient discriminating parameter: values of α significantly smaller than 0.5 correspond to a concerted mechanism [17,18]. Investigations on the dynamics of dissociative electron transfer to a large number of organic halides have already been reported, showing that alkyl halides undergo a concerted mechanism and are characterized by small α values [16,19–24]. Analysis of the dependence of E_p and half-peak width ($E_p - E_{p/2}$) on scan rate [16] gives α values of 0.31 and 0.28 for TCA and DCA, respectively, which are indicative of a concerted dissociative electron transfer (ET). Therefore, in analogy with most alkyl halides and PCMs in particular, the following reduction mechanism may be proposed for TCA and DCA (reactions (4)–(9)):



where HB may be the residual water in the solvent, the background electrolyte, PCA itself or any added proton donor. In line with the above mechanism, it appears that reduction of TCA and DCA occurs by sequential removal of a chlorine atom up to complete dechlorination to ethane.

The voltammetric pattern of TCA at Cu (Fig. 1 B, solid line) shows two reduction peaks at -1.91 V and -2.65 V vs SCE, the latter being identical to the reduction peak observed for an authentic sample of DCA (dashed line). It is important to note that cyclic voltammetry of DCA does not show any evidence of a reduction peak attributable to CA. However, it is possible to observe that the current intensity of the second peak ($30 \mu\text{A}$) of TCA is considerably higher than that of the first peak ($20 \mu\text{A}$). Since reduction of each polychloroethane to the immediately less chlorinated compound involves two electrons, one would expect a series of peaks of almost the same height. We may assume that CA is reduced at a potential similar to or more positive than that of DCA and hence the single reduction peak observed for DCA is composed of two overlapping peaks, one for

the starting molecule and one for its reduction product CA, which would explain why this peak is much higher than that of TCA. Analysis of the voltammetric data at Cu gave very small α values for both TCA (0.24) and DCA (0.26), indicating that a concerted mechanism is followed, i.e. simultaneous electron transfer and C–Cl bond breaking, just like what was already observed at GC.

A comparison between the reduction peaks of TCA recorded at Cu and GC electrodes (Table 1) shows a positive shift of ca. 0.2 V for Cu, which testifies the catalytic nature of this electrocyclic material. The catalytic effect expressed as $\Delta E_p^{\text{cat}} = E_p^{\text{Cu}} - E_p^{\text{GC}}$ is quite modest in the case of DCA (only 0.07 V), and in general ΔE_p^{cat} for PCAs is found to be lower than that already observed for the analogous molecules CHCl_3 and CH_2Cl_2 of the homologues series. In Fig. S1 a comparison between the ΔE_p^{cat} values measured for PCAs and PCMs is illustrated and it is clear that reduction of the latter at Cu occurs with a catalytic effect almost 0.3 V higher than reduction of PCAs in the same conditions. Addition of a weak proton donor such as water slightly affects ΔE_p^{cat} for PCAs in agreement with what was already observed for PCMs. On the other hand, addition of HAC induces a huge enhancement of the ΔE_p^{cat} to 0.82 V in the case of TCA, while it seems to slightly decrease the catalytic effect for the reduction of DCA due to an anodic shift of E_p at GC (Table 1).

As a partial conclusion, PCAs have shown at Cu a voltammetric behavior similar to that of PCMs both in the presence and absence of a proton donor. This suggests that the two series of chlorinated VOCs undergo similar dehalogenation mechanisms. On the other hand, a comparison between the ΔE_p^{cat} values at Cu indicates that modification of the molecular structure, i.e. substitution of a H atom with a more bulky methyl group, may play a key role in the activation of carbon–chlorine bonds, probably in terms of interactions of the starting substrate and its reduction intermediates with the electrode surface.

3.2. Controlled-potential electrolyses

The voltammetric analyses in DMF + 0.1 M Pr_4NBF_4 suggest that reduction of PCAs follows a hydrodechlorination mechanism. However, it is wise to have a confirmation of these findings in preparative scale electrolysis, which unlike voltammetry allows identification of the intermediates and products and monitoring of their evolution during the experiment. Furthermore, electrolysis experiments represent a sort of stress test for the electrodes and are therefore useful to check whether the electrochemical activity of Cu remains stable all over the experiment or suffers from some fouling problems.

Stepwise electrolysis of TCA was carried out by fixing the potential after the first reduction peak of TCA but before that of DCA to avoid reduction of the latter during this stage of electrolysis. When the current dropped to below 5% of its initial value, the applied potential was shifted to a potential corresponding to the reduction of DCA and was kept constant up to the end of the electrolysis. In this manner, a sequential reduction of the starting substrate and its principal reduction product was achieved in two separate steps. The complete reduction of the starting TCA and of its intermediates was confirmed by voltammograms recorded during the electrolysis. Electrolyses of DCA were carried out at only one fixed potential located after its single reduction peak. The results of all electrolysis experiments performed at Cu, both in the presence and absence of HAC or added H_2O , are summarized in Tables 2 and 3. The concentration of HAC was fixed at 0.1 M , whereas the concentration of H_2O was 1 M . H_2O is a much weaker proton donor than HAC, therefore a large excess had to be used in order to ensure fast protonation of electrogenerated anions. However, the concentration of H_2O was limited to 1 M in order to avoid the superimposition of its discharge with the reduction of DCA. Some comparative experiments for TCA were also carried out by applying a fixed potential

Table 2Electrolyses of CH_3CCl_3 (10 mM) in 20 mL of DMF + 0.1 M Pr_4NBF_4 at a Cu cathode.^a

Entry	Substrate	E_{app}^b (V)	n^c	CH_3CCl_3 (%)	CH_3CHCl_2 (%)	$\text{CH}_3\text{CH}_2\text{Cl}$ (%)	CHCl_3 (%)	CH_3CH_3 (%)	CH_2CH_2 (%)	CHCH (%)
1a	TCA	−2.25	1.68	0	59.9	0	4.9	0.1	0.1	9.0
1b		−2.75	3.84	0	0	0	0	16.7	15.5	0.5
2	TCA	−2.75	2.02	0	20.1	1.2	11.8	0.9	0.22	1.4
		−2.75	4.09	0	0	0	0	18.1	18.5	5.32
3a	TCA + H_2O^d	−2.00	1.70	0	48.7	0	21.8	0.1	0.1	3.5
3b		−2.65	5.73	0	0	2.5	0	39.8	16.1	1.1
4	TCA + H_2O^d	−2.65	2.0	0	18.0	4.2	29.5	17.7	5.4	23.7
		−2.65	6.0	0	1.6	0	0	36.4	64.4	0
5a	TCA + HAc^e	−1.75	3.02	1.2	84.7	0.0	0	2.8	0.5	0
5b		−2.55	9.2	0	0	0	0	72.5	4.5	0
6	TCA + HAc^e	−2.55	5.84	5.1	43.6	6.0	0	18.6	4.5	0
		−2.55	8.76	0	15.5	8.7	0	31.7	5.1	0
		−2.55	11.19	0	0	0	0	59.3	6.4	0

^a Values in percentage were calculated with respect to the starting substrate.^b Applied potential vs SCE.^c Electrons transferred per molecule.^d In the presence of 1 M H_2O .^e In the presence of 100 mM $\text{CH}_3\text{CO}_2\text{H}$.

corresponding to that of its second reduction peak (see Fig. 1B). This was aimed to evaluate whether the operating mode of electrolysis (fixed potential vs variable potential) can influence the product distribution.

In Fig. 2 are reported the principal reduction products of TCA observed during preparative electrolysis at Cu in DMF + 0.1 M Pr_4NBF_4 in the absence and presence of added proton donors. For the sake of simplicity and convenience we start to describe the results of the controlled-potential electrolysis carried out in the presence of HAc . Fig. 2a clearly shows that upon consumption of TCA during the first step, there is accumulation of DCA, which in turn decreases during the second step while CA slightly increases. In particular, after almost complete reduction of TCA, 84.7% of DCA was obtained together with a small quantity (2.8%) of CH_3CH_3 (Table 2, entry 5a). Once the potential was switched to −2.55 V vs SCE, reduction of DCA became the principal electrode process, resulting in the formation of ethane as the main product (ca 73%) together with a small amount (<5%) of ethylene (Table 2, entry 5b). It is worth noting that the formation of CH_3CH_3 in this second step clearly indicates that CA is reducible at this potential. The trend of CA concentration (Fig. 2A), which passes through a low maximum (yield < 5%), is supportive of the assumption that reduction of CA occurs at Cu concomitantly with that of DCA. According to these findings and considering that other chlorinated intermediates were not detected, reduction of TCA in DMF + 0.1 M Pr_4NBF_4 + 0.1 M HAc follows almost exclusively a hydrodechlorination mechanism, i.e. conversion of TCA to ethane occurs through a series of reduction steps each involving two electron transfers, removal of a chloride

ion and protonation (Scheme 1, pathway a). However, the small amount of ethylene detected is indicative of the presence of another reduction mechanism. Along with ethane and ethylene, 1-butene (5.2%), and 1,3-butadiene (5.4%) were found in the gas phase.

In Fig. 2B the main reduction products of TCA in the presence of 1 M H_2O are reported. In comparison with the electrolysis performed in the presence of HAc , the yield of ethane decreased to 39.8%, whereas that of ethylene increased to 16.1% (Table 2, entry 3b). More interestingly, chloroacetylene (CI) along with dichloroethylene (DCE) and chloroethylene (CE) were found as intermediate products. These findings clearly point out that although hydrodechlorination still remains the principal reaction route in the presence of H_2O , some side reactions gain in importance. In contrast to H_2O , chlorinated unsaturated species were not detected when the more strong acid (HAc) was used. The formation of chlorinated ethylene and acetylene in the presence of H_2O may be explained by a dehydrodehalogenation mechanism, which involves the elimination of H^+ and Cl^- and the formation of a double or triple bond as illustrated in Scheme 1, (pathways b and c). In the proposed mechanism, the α , β -elimination is promoted by a base (B^-). To verify the importance of a base-promoted α , β -elimination in our experimental conditions, 2×10^{-4} mol of Bu_4NOH were added to a solution containing 2×10^{-4} mol of TCA (10 mM) in DMF + 0.1 M Pr_4NBF_4 and the mixture was electrolyzed as usual (see Fig. 3). The addition of OH^- at open circuit (Fig. 3, 0.0 electrons transferred) led to the disappearance of more than 50% of the starting TCA and the formation of DCE (23.6%) and CI (18.4%), while neither ethylene nor acetylene was detected.

Table 3Electrolyses of CH_3CHCl_2 (10 mM) in 20 mL of DMF + 0.1 M Pr_4NBF_4 at a Cu cathode.^a

Entry	Substrate	E_{app}^b (V)	n^c	CH_3CHCl_2 (%)	$\text{CH}_3\text{CH}_2\text{Cl}$ (%)	CH_2CHCl (%)	CH_3CH_3 (%)	CH_2CH_2 (%)	CHCH (%)
1a	DCA	−2.75	1.01	30.3	2.5	1.1	9.2	1.6	18.2
1b		−2.75	2.68	0	0	0	20.8	14.9	0.0
2	DCA + H_2O^d	−2.65	3.01	3.5	7.9	3.6	48.0	0.8	15.6
		−2.65	5.05	0	0	0	56.1	5.4	3.6
3	DCA + HAc^e	−2.55	4.04	52.4	9.2	0	18.5	1.6	0
		−2.55	9.65	0	0	0	84.2	6.4	0

^a Values in percentage were calculated with respect to the starting substrate.^b Applied potential vs SCE.^c Electrons transferred per molecule.^d In the presence of 1 M H_2O .^e In the presence of 100 mM $\text{CH}_3\text{CO}_2\text{H}$.

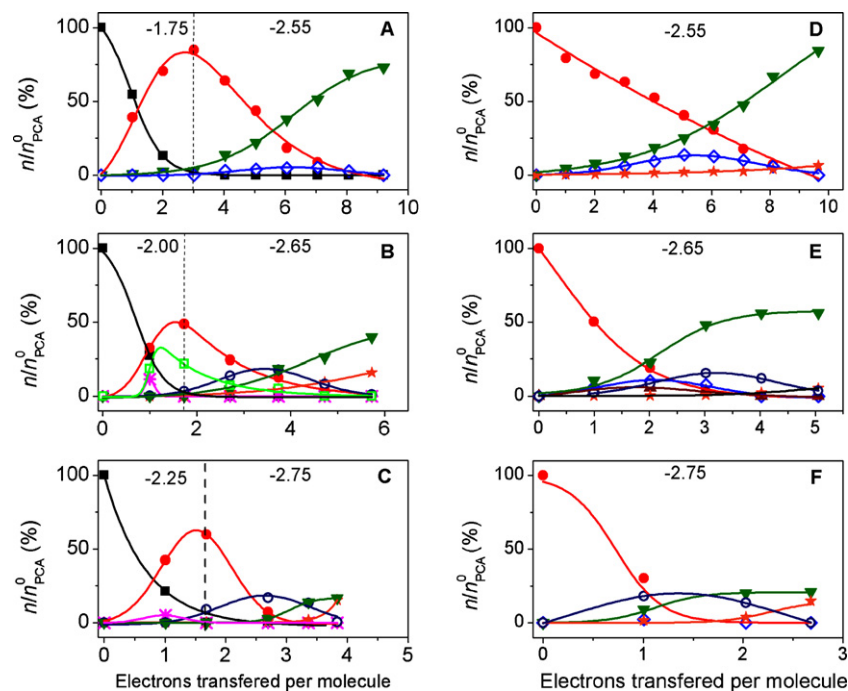
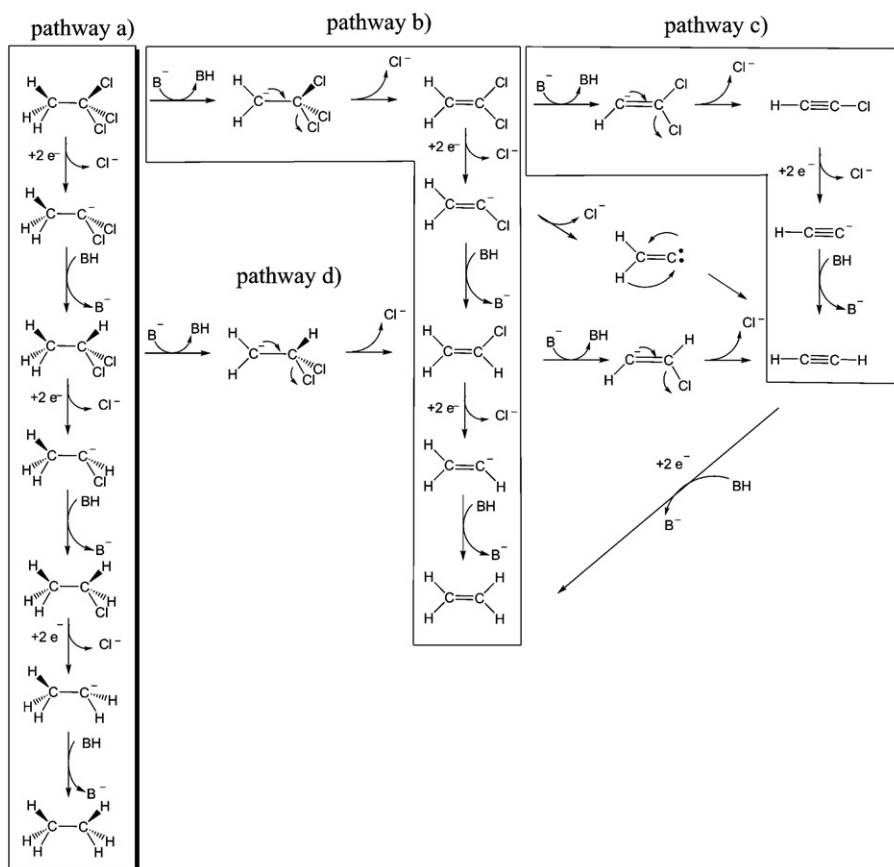


Fig. 2. Main intermediates detected during stepwise electrolysis of $10\text{ mM } CH_3CCl_3$ (A–C) and fixed-potential electrolysis of $10\text{ mM } CH_3CHCl_2$ (D–F) performed at Cu in DMF + $0.1\text{ M } Pr_4NBF_4$, in the presence of either $0.1\text{ M } CH_3CO_2H$ (A, D) or $1\text{ M } H_2O$ (B, E), or in the absence of any added proton donor (C, F): (\blacksquare) CH_3CCl_3 , (\bullet) CH_3CHCl_2 , (\diamond) CH_3CH_2Cl , (\ast) CH_2CCl_2 , (\blacktriangle) CH_2CHCl , (\square) $CHCCl$, (\blacktriangledown) CH_3CH_3 , (\star) CH_2CH_2 , (\circ) $CHCH$. The inserted numbers indicate E_{app} , whereas the vertical lines indicate when it was changed.



Scheme 1. Reaction scheme for the reduction of polychloroethanes.

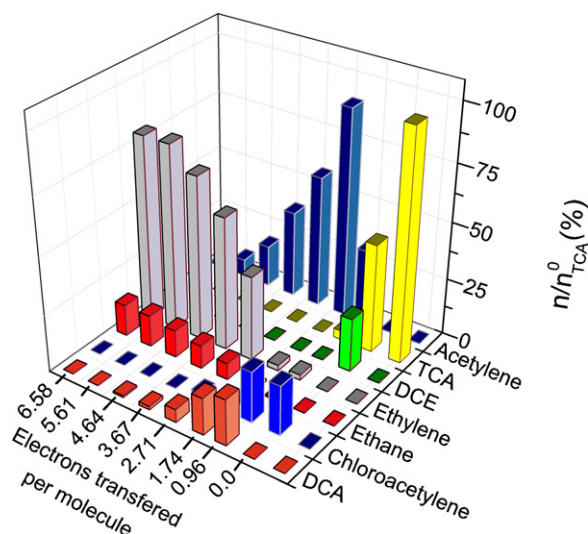


Fig. 3. Main intermediates detected during the stepwise electrolysis of 10 mM CH_3CCl_3 at Cu in DMF + 0.1 M Pr_4NBF_4 in the presence of 10 mM Bu_4NOH added before electrolysis.

Electrolysis of the remaining TCA allowed the complete reduction of the starting substrate with the accumulation of acetylene (90%) as an intermediate and final conversion of TCA to ethylene (80%) and ethane (14%). These findings confirm that the presence of a base prompts the dehydrodechlorination mechanism to the detriment of the hydrodechlorination route; these data also confirm that acetylene and ethylene are products of the electrochemical reduction, the latter arising from reduction of the former.

The experiments with 1 M H_2O have shown that H_2O plays the role of proton donor, enhancing the yields of hydrodehalogenation products as compared to the electrolyses without added proton donors. On the other hand, however, the presence of H_2O promotes a reaction route involving a base (Scheme 1, pathways b and c). This base is presumably OH^- ions generated near the electrode surface when carbanion intermediates are protonated by H_2O molecules (Eq. (3)) or directly electrogenerated at the electrode by electrolysis of H_2O . The latter route becomes important only in the later stages of electrolysis when E_{app} values close to the cathodic discharge limit are applied. Thence, on the basis of these results we may guess that the starting TCA is deprotonated to $\text{Cl}_3\text{CCH}_2^-$ by OH^- and the so generated carbanion can undergo Cl^- elimination to give DCE (Scheme 1, pathway b). DCE can in its turn be exhaustively reduced at the electrode surface till complete dehalogenation to ethylene. However, the detection of chloroacetylene during the electrolysis or after the addition of a strong base indicates that DCE can undergo further α,β -elimination leading to chloroacetylene (Scheme 1, pathway c) which can be reduced to acetylene according to a hydrodechlorination mechanism. It is thence evident that H_2O plays a double role in the electrolysis of TCA at Cu: on one hand it favors the hydrodehalogenation mechanism by the protonation of electrogenerated carbanions; on the other hand, it generates OH^- which promotes the dehydrodechlorination mechanism. Another point to be stressed is that although both TCA and DCE are very weak C–H acids, the deprotonation reactions proceed thanks to the following irreversible Cl^- eliminations leading to stable products.

In the presence of H_2O , father–son type reactions are hampered because H_2O is a far stronger acid than either TCA or DCA, but these reactions would not be negligible if a proton donor stronger than the PCE is not added. In Fig. 2E are reported the principal reduction products of TCA without any intentionally added proton donor; in this case only low yields of ethane (16.7%) and ethylene (15.5%) were obtained at the end of the electrolysis (Table 2, entry 1b). It

can be observed, however, that in the first step of the electrolysis 59.9% of DCA together with 9% of acetylene and small amounts of Cl (4.9%) were obtained. The product yield trends of this electrolysis show that at $E_{\text{app}} = -2.25$ V, reduction of TCA mainly follows a hydrodehalogenation pathway leading to DCA as the principal product. The process becomes more complicated at $E_{\text{app}} = -2.75$ V (Table 2, entries 1b and 2); neither hydrodehalogenation nor dehydrodehalogenation is the dominant reaction route. In addition, the results cannot be rationalized by considering only these two reaction pathways. Therefore the low yields of ethane and ethylene and the loss of carbon mass balance during the electrolysis suggest that other side reactions become important. In particular, a non-negligible amount (11%) of C_4 hydrocarbons (butane, 2-butene, 1,3-butadiene) was detected at the end of electrolysis. Formation of C_4 was also observed in the presence of HAC or H_2O , the respective total C_4 yields being 12% and 5%. To explain the formation of C_4 , we examined the electrochemical reduction of C_2H_2 at Cu in DMF + 0.1 M $(\text{C}_3\text{H}_7)_4\text{NBF}_4$. Acetylene exhibits one irreversible reduction peak at -2.38 V and when controlled-potential electrolysis was performed at $E_{\text{app}} = -2.40$ V, ethylene, 2-butene and 1,3-butadiene were found as principal products, while ethane and butane were not detected. Furthermore, the yield profile recorded for 1,3-butadiene during electrolysis showed a bell-shaped trend, indicating the presence of a consecutive reaction, which was found to be reduction of 1,3-butadiene to 2-butene. This means that during electrolysis of TCA, acetylene is effectively reduced first to 1,3-butadiene and then to 2-butene and that ethylene is not converted to ethane. The formation of butane may be due to reduction of chlorobutane, but there is no clear evidence of the formation of this substrate during the experiment.

Electrolyses of DCA at Cu show similar trends as those described for TCA and the results are summarized in Table 3, whereas the concentration profiles of the main intermediates and products are illustrated in Fig. 2D–F. At $E_{\text{app}} = -2.75$ V vs SCE, DCA is mainly reduced to acetylene, which is then reduced to ethylene (Fig. 2D, Table 3, entry 1). During electrolysis CA was detected only in low percentages (2–3%), but the final yield in ethane (20.8%), which presumably arises from hydrodehalogenation of CA, suggests that the latter was effectively formed as an intermediate that could not accumulate because of the highly negative E_{app} at which it is readily reduced. When the electrolysis was repeated in the presence of 1 M H_2O (Fig. 2E, Table 3, entry 2), ethane (56.1%) was obtained as the main reduction product, which indicates that hydrodechlorination is the predominant reaction pathway. However, the detection of chloroethylene (3.6%) and the accumulation of acetylene (15.6%) point out that DCA reduction follows also the dehydrodechlorination mechanism. The low yield of ethylene (5.4%) suggests that this substrate is probably the direct product of the reduction of chloroethylene produced according to pathway (d) of Scheme 1. In the presence of 0.1 M HAC (Fig. 2F, Table 3, entry 3) the yield in ethane became even higher (84.2%), while acetylene was hardly detectable and the final yield of ethylene dropped to 6.4%. The results of the electrolyses of DCA are in agreement with what was already observed and discussed for TCA. Also in this case 2-butene and 1,3-butadiene were detected (<6%) as a result of acetylene reduction.

Single step potentiostatic electrolyses were carried out to check whether the applied potential has a substantial effect on the nature of the intermediates and the distribution of the products. This type of experiment is particularly interesting for possible applications where the change of the applied potential during the process is not possible or requires burdening costs. In fact, one step electrolysis has the advantage of working with higher current density as compared to multi-step electrolyses and hence the experiment lasts in a much shorter time. Some electrolyses of TCA were carried out at Cu at -2.75 V vs SCE and at -2.65 V and -2.55 V vs

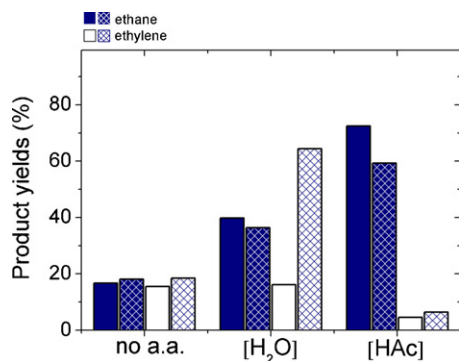


Fig. 4. CH_3CH_3 and CH_2CH_2 yields from exhaustive electrolyses of CH_3CCl_3 performed at Cu in DMF + 0.1 M Pr_4NBF_4 in the absence and presence of either 0.1 M HAc or 1 M H_2O . The patterned and non-patterned columns correspond to one-step and stepwise electrolyses, respectively.

SCE in presence of 1 M H_2O and 0.1 M HAc, respectively (Table 2, entries 2,4,6). Concentration profiles for the starting reagent as well as its reduction intermediates and products, recorded during electrolysis, are illustrated in Fig. S2. The results show that accumulation of DCA is less favorable with respect to the sequential electrolysis because at the applied potential the starting substrate and its reduction intermediates are reduced simultaneously. It is interesting to note that in the case of the electrolyses conducted at the last peak potential, C_4 yields drop to less than 3% both in the presence and absence of any added proton donor (data not shown in Table 2). Therefore, coupling of intermediates arising from acetylene reduction to give C_4 becomes partially suppressed when the electrolysis is conducted at a sufficiently negative potential.

A last comment on the one-step potentiostatic electrolyses is on the production of ethane and ethylene. As shown in Fig. 4 the yield of ethane increases with the increase of the proton availability in solution, the presence of 0.1 M HAc providing the best conditions for obtaining high yields of ethane both in the stepwise and one-step electrolyses. Moreover, in the latter case the production of ethane and ethylene was found to start at the beginning of the electrolysis and increase steadily during the whole experiment. In the absence of any added proton donor, the yield of CH_3CH_3 was almost unaffected by how the electrolysis is performed (Table 2, entries 1 and 2). This is true also when H_2O was used as a proton donor (Table 2, entries 3 and 4), whereas the yields were slightly different when HAc was used as the proton source (Table 2, entries 5 and 6). Thence, the selectivity of ethane production is not particularly affected by switching periodically the potential. The same considerations can be made also in the case of ethylene, but not when H_2O is used as a proton source. In fact, in this case the yield of ethylene was found to increase from 16% in the stepwise electrolysis to 64% in the one-step electrolysis (Table 2, entries 3 and 4). Ethylene is formed via dehydrodechlorination, which is prompted by the presence in solution of a strong base such as OH^- . Therefore, an enhanced yield of ethylene may be justified by an increased concentration of OH^- . This is quite reasonable since the applied potential (-2.65 V vs SCE) is close to the solvent discharge, where the concomitant electrolysis of H_2O may take place to produce hydroxyl anions:



4. Conclusions

In this study it was demonstrated that Cu allows the exhaustive electrochemical degradation of highly toxic PCAs to ethane and

ethylene under fairly mild conditions. Electroreduction of TCA and DCA follows preferentially the hydrodechlorination mechanism only in the presence of a proton donor such as HAc or H_2O . Addition or electrogeneration of a strong base such as OH^- to the solution promotes a dehydrodechlorination mechanism in which TCA is degraded to dichloroethylene and chloroacetylene, without the consumption of any charge. It is important to note, however, that a base-promoted dehydrodechlorination cannot give a complete degradation of PCAs, which instead can be effectively achieved only if the partially degraded intermediates such as dichloroethylene and chloroacetylene are reduced to ethylene and acetylene at a Cu cathode. Furthermore, we have observed that at Cu acetylene is reduced to ethylene but not to ethane. This establishes that ethane and ethylene are the end points of two completely different reduction pathways.

Another important outcome of this study is that the catalytic activity of Cu for the reduction of PCAs is not as good as the one observed for the reduction of PCMs, which suggests a deep influence of the chemical structure of the target molecules on the catalytic activity of the surface. The catalytic activity of Cu for the reduction of TCA is enhanced by the presence of a good proton donor but not by the addition of H_2O . The presence of HAc or H_2O affects drastically the yields of ethane and ethylene for the reduction of both TCA and DCA. In fact, in the presence of HAc the ethane yields exceed 70–80%, whereas when the electrolysis was carried out in the presence of H_2O and at a sufficiently negative potential high yields (>60%) of ethylene were obtained.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2012.07.003>.

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